

Whole Air Sampling and Analysis during the Spring 2006 NASA INTEX-B/MILAGRO Missions

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During the spring 2006 INTEX-B/MILAGRO missions our group will collect up to 168 whole air samples per flight aboard the DC-8 aircraft, using the same successful sampling equipment and strategy as during INTEX-A. Each sample will be analyzed at our University of California, Irvine (UCI) laboratory for more than 60 trace gases including C₂-C₁₀ NMHCs, C₁-C₂ halocarbons, C₁-C₅ alkyl nitrates, and carbonyl sulfide (OCS) (see Table). All gases will be reported at detection limits and time resolutions that are at or better than those requested in the list of flight measurement priorities for INTEX-B/MILAGRO.

During each flight air samples will be collected into individual 2-L stainless steel canisters each equipped with a bellows valve. Seven canister arrays, each consisting of 24 canisters that are embedded in foam and linked together (called a “snake”), will be loaded onto the aircraft before each flight. Prior to the mission the canisters will be conditioned, evacuated, and 10 Torr of degassed distilled water will be added to each canister to quench active surface sites. During sampling, outside air will be collected from beyond the laminar boundary layer of the aircraft via a window-mounted, forward-facing ¼-inch stainless steel inlet. The sample air will be pressurized by a two-stage metal bellows pump, and distributed via ¼-inch stainless steel tubing to a gas-handling manifold. The pump uses 60 Hz power and draws about 10 A (110 V) while running and 30 A at power-up. The gas-handling manifold allows the air to be selectively directed into any given canister, and sample air will be collected until a pressure of 40 psig is reached inside the canister. An aft-facing outlet will be used to exhaust uncollected air.

The whole air samples will be collected throughout each flight, at an anticipated rate of every 4-5 minutes during horizontal flight legs, and every 1-2 minutes during ascents and descents. Sample collection aboard the aircraft will be coordinated with other experiments and any intercomparison activities, so as to optimize sample overlap with other groups. Our sampling strategy also includes the flexibility for discretionary “samples of opportunity” during interesting or unexpected air mass encounters. A mass flow controller allows us to compensate for external pressure changes and therefore to control the time it takes for the canister to fill. The sample collection times usually range from 30 seconds to 2 minutes. The longer collection times are used on horizontal flight legs for better spatial coverage, and shorter sampling times on vertical flight legs in order to maximize the vertical resolution. Based upon typical cruising velocities of 830-850 km hr⁻¹ during horizontal flight legs, a 2 minute collection time covers a sampling distance of roughly 28 km. The vertical sampling distances are on the order of several hundreds of meters.

After each flight, the filled canister arrays will be removed and shipped to our laboratory at UC-Irvine for analysis within seven days of being collected. Two analytical will be operated around the clock to improve canister turn-around time and to keep our measurement precision optimal. Two electron capture detectors (ECDs, sensitive to halocarbons and alkyl nitrates), three flame ionization detectors (FIDs, sensitive to hydrocarbons), and a quadrupole mass spectrometer detector (MSD, for unambiguous compound identification, selected ion monitoring) will be employed. For each sample, 2015 ± 2 mL (STP) of canister air will be used

for analysis, as follows. The condensable trace gases (including all hydrocarbons except CH₄) are preconcentrated in a loop that is filled with glass beads and immersed in liquid nitrogen. The loop is then isolated before being warmed (~80°C) to revolatilize the gases. The contents of the loop are flushed using a hydrogen carrier gas and are quantitatively split to the six different columns. The first column-detector combination is a DB-5ms column (J&W; 60 m, 0.25 mm I.D., 0.5 µm film thickness) output to a quadrupole MSD (HP-5973). The second combination is a DB-1 column (J&W; 60 m, 0.32 mm I.D., 1 µm film thickness) output to an FID (HP-6890). The third combination is a PLOT column (J&W GS-Alumina; 30 m, 0.53 mm I.D.) connected in series to a DB-1 column (J&W; 5 m, 0.53 mm I.D., 1.5 µm film thickness) and output to an FID. The fourth combination is a RESTEK 1701 column (60 m, 0.25 mm I.D., 0.50 µm film thickness) which is output to an ECD. The fifth combination is a DB-5 (J&W; 30 m, 0.25 mm I.D., 1 µm film thickness) column connected in series to a RESTEK 1701 column (5 m, 0.25 mm I.D., 0.5 µm film thickness) and output to an ECD. The sixth is a Cyclodex column (J&W; 60 m, 0.25 mm I.D., 0.25 µm film thickness) output to an FID. The fractional split to each column will be determined from standards run intermittently with the air samples (every fourth sample).

The baselines on each chromatogram will be individually inspected for selected compounds, including 30 C₂-C₁₀ NMHCs, 20 C₁-C₂ halocarbons, 7 C₁-C₅ alkyl nitrates, and OCS. The range of accuracies for these gases is 2-20%. The precision of the halocarbon measurement varies by compound and by mixing ratio. For example, the precision for CFC-12 at 540 pptv is ±3 pptv, while that for methyl iodide (CH₃I) at 0.02 pptv is ±0.005 pptv. The measurement precision for the NMHCs is approximately 1% or 1.5 pptv (whichever is larger) for the alkanes and alkynes, and 3% or 3 pptv (whichever is larger) for the alkenes. The alkyl nitrate precision is 3% for mixing ratios above 5 pptv and 5% for mixing ratios below 5 pptv. The OCS precision is 2%. The limit of detection (LOD) is different for each halocarbon, but none of the 20 halocarbons that we will quantify are expected to be below their detection limit at any time during INTEX-B. We impose a conservative LOD of 3 pptv for the NMHCs. The alkyl nitrate LOD is 0.01 pptv, and the OCS detection limit is 10 pptv. Calibration is an ongoing process, whereby new standards are referenced to older certified standards, with appropriate checks for stability, and also with occasional inter-laboratory comparisons.

Gases we will quantify during INTEX-B/MILAGRO.

Ethane	2-Methylpentane	DMS	CCl ₃ F (CFC-11)
Ethene	3-Methylpentane	OCS	CCl ₂ F ₂ (CFC-12)
Ethyne	Benzene	Methyl Nitrate	CCl ₂ FCClF ₂ (CFC-113)
Propane	Toluene	Ethyl Nitrate	CClF ₂ CClF ₂ (CFC-114)
Propene	<i>o</i> -Ethyltoluene	1-Propyl Nitrate	CH ₃ Cl
<i>n</i> -Butane	<i>m</i> -Ethyltoluene	2-Propyl Nitrate	CH ₂ Cl ₂
<i>i</i> -Butane	<i>p</i> -Ethyltoluene	2-Butyl Nitrate	CHCl ₃
1-Butene	1,2,4-Trimethylbenzene	2-Pentyl Nitrate	CCl ₄
<i>cis</i> -2-Butene	1,3,5-Trimethylbenzene	3-Pentyl Nitrate	CH ₃ CCl ₃
<i>trans</i> -2-Butene	<i>o</i> -Xylene	CH ₂ FCF ₃ (HFC-134a)	C ₂ HCl ₃
1,3-Butadiene	<i>m</i> -Xylene	CH ₃ CCl ₂ F (HCFC-141b)	C ₂ Cl ₄
<i>n</i> -Pentane	<i>p</i> -Xylene	CH ₃ CClF ₂ (HCFC-142b)	CH ₃ Br
<i>i</i> -Pentane	Ethylbenzene	CHClF ₂ (HCFC-22)	CH ₂ Br ₂
Isoprene	α-Pinene	CBrClF ₂ (H-1211)	CHBr ₃
<i>n</i> -Hexane	β-Pinene	1,2-DCE	CH ₃ I

